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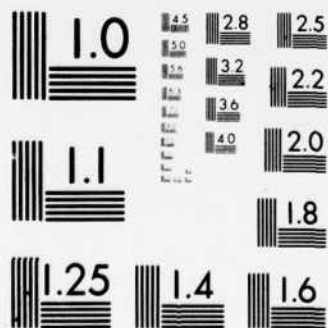


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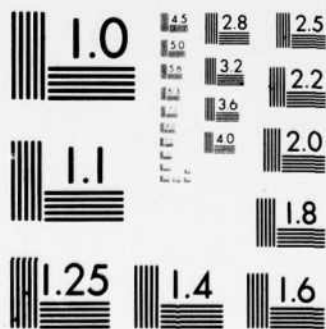


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Detailed Structure of Bis- $\mu$ -(trimethylsilylmethylidyne)

tetrakis-(trimethylsilylmethyl)ditungsten(W-W).

by M.H. Chisholm,<sup>1a</sup> F.A. Cotton,<sup>1b\*</sup> M. Extine,<sup>1b</sup>

and C.A. Murillo<sup>1a</sup>

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each residing on a crystallographic inversion center. The two crystallographically independent W-W distances,  $2.521(2)\text{\AA}$ , and  $2.549(2)\text{\AA}$ , are consistent with the presence of W-W single bonds. The basic crystallographic data are as follows. Space group,  $P2_1/a$ . Unit cell dimensions:  $a = 11.976(4)\text{\AA}$ ;  $b = 18.989(5)\text{\AA}$ ;  $c = 18.111(5)\text{\AA}$ ;  $\beta = 101.02(2)^\circ$ ;  $V = 4043(2)\text{\AA}^3$ ;  $Z = 4$ .

Contribution from the Departments of Chemistry  
Texas A&M University, College Station, Texas 77843  
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Detailed Structure of Bis- $\mu$ -(trimethylsilylmethyldiyn)tetraakis-  
(trimethylsilylmethyl)ditungsten(W-W).

M. H. Chisholm,<sup>1a</sup> F. A. Cotton,<sup>1b\*</sup> M. Extine,<sup>1b</sup> and C. A. Murillo<sup>1a</sup>

ABSTRACT

The crystal and molecular structures of a compound of composition  $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$  have been determined. The compound consists of dinuclear molecules which contain bridging alkylidyne groups,  $CSiMe_3$ , which, along with the tungsten atoms form planar, rhombic rings,  $\overline{W-C-W-C}$ . Two alkyl groups,  $CH_2SiMe_3$ , are attached to each metal atom to form distorted tetrahedra about the metal atoms. There are two crystallographically independent molecules, each residing on a crystallographic inversion center. The two crystallographically independent W-W distances,  $2.521(2)\text{\AA}$  and  $2.549(2)\text{\AA}$ , are consistent with the presence of W-W single bonds. The basic crystallographic data are as follows. Space group,  $P2_1/a$ . Unit cell dimensions:  $a = 11.976(4)\text{\AA}$ ;  $b = 18.989(5)\text{\AA}$ ;  $c = 18.111(5)\text{\AA}$ ;  $\beta = 101.02(2)^\circ$ ;  $V = 4043(2)\text{\AA}^3$ ;  $Z = 4$ .

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## INTRODUCTION

In a previous study<sup>2</sup> we attempted to prepare  $W_2(CH_2SiMe_3)_6$ <sup>3</sup> from the reaction between  $WCl_4$  and  $Me_3SiCH_2MgCl$  (1:4 mole ratio) and fortuitously isolated a new compound which we formulated,<sup>2</sup> on the basis of noncrystallographic evidence, as bis-μ-(trimethylsilylmethylidyne)tetrakis(trimethylsilylmethyl)ditungsten,  $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$ , I. We proposed this structure by analogy to that found<sup>4</sup> for  $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$  but explicitly noted that the ditungsten compound should contain a metal-to-metal bond.  $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$  has also been prepared independently,<sup>5</sup> and the same structure proposed.

We report here the results of a single crystal x-ray study on I that confirms the structure proposed for it.

## EXPERIMENTAL SECTION

The method we used for the preparation of I has been described previously.<sup>2</sup> Crystals of I were grown from pentane at ca. -78°C. Reactions of I with  $C_2H_2$ ,  $MeCCMe$ ,  $PhCCH$ ,  $MeO_2CC_2CO_2Me$ ,  $C_3H_4$ ,  $C_2H_4$ , 1,3-butadiene, and  $CO_2$  were carried out in 5 mm NMR tubes in toluene- $d_8$ . Gaseous reagents were added to solutions of I using vacuum line techniques. Other reagents were added to the NMR tubes by syringe. The progress of the reactions was monitored via  $^1H$  NMR spectroscopy. No attempt was made to isolate any of the products of these reactions.

### X-Ray Crystallography. Crystal Selection and Data Collection.

Considerable difficulty was encountered in (i) mounting crystals of  $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$  in such a manner that they did not decompose and (ii) once they were mounted, finding a crystal of suitable quality. Finally, a platelike crystal measuring ca. 0.17 x 0.34 x 0.56 mm was mounted by wedging it into a nitrogen-filled capillary in a glove box. The ends of the capillary were

sealed with a small hand torch. The crystal was mounted with its longest dimension nearly coincident with the  $\phi$  axis. Omega scans of several intense low-angle reflections had peak widths at half-height of ca.  $0.2^\circ$ . Lattice constants and axial photographs indicated that the crystal belonged to the monoclinic system. The unit cell constants, determined from the setting angles of 15 reflections having  $21^\circ < 2\theta_{\text{MoK}\alpha} < 27^\circ$  are:  $a = 11.976(4)\text{\AA}$ ,  $b = 18.989(5)\text{\AA}$ ,  $c = 18.111(5)\text{\AA}$ ,  $\beta = 101.02(2)^\circ$ , and  $V = 4043(2)\text{\AA}^3$ . The observed volume was consistent with that expected for  $Z = 4$ . The systematic absences observed during data collection,  $0k0$  ( $k = 2n+1$ ) and  $h0l$  ( $h = 2n+1$ ) uniquely determined the space group to be  $P2_1/a$  (equiv. positions  $\pm \{x, y, z; 1/2-x, 1/2+y, -z\}$ ) a non-standard setting of  $P2_1/c$  (No. 14).

The data were collected at  $25^\circ\text{C}$  with a Snytex P1 autodiffractometer equipped with a graphite crystal monochromator and using  $\text{MoK}\alpha$  ( $\lambda = 0.710730\text{\AA}$ ) radiation. Variable scan rates from  $4.0$  to  $24.0^\circ/\text{min}$  were used for symmetric  $\theta/2\theta$  scans ranging from  $1.0^\circ$  below to  $1.0^\circ$  above the calculated  $\text{MoK}\alpha_1$ - $\text{K}\alpha_2$  doublet. The ratio of scan to background time was  $0.5$ . A total of  $5313$  unique, non-systematically absent reflections having  $0^\circ < 2\theta_{\text{MoK}\alpha} < 45.0^\circ$  were recorded. The intensities of three standard reflections were monitored frequently throughout data collection and showed no decrease in intensity. The data were reduced to a set of relative  $|F_o|^2$  values.<sup>6</sup> The intensities were corrected for absorption effects ( $\mu = 62.1\text{ cm}^{-1}$ ); transmission coefficients ranged from  $0.160$  to  $0.394$  with an average of  $0.285$ . The  $2396$  data having  $I > 3\sigma(I)$  were retained as observed and used in subsequent structure solution and refinement.

Structure Solution and Refinement.<sup>6</sup> The positions of the  $32$  unique non-hydrogen atoms were determined by standard heavy atom methods. The structure was refined to convergence using anisotropic thermal parameters for the tungsten and silicon atoms and isotropic thermal parameters for the carbon atoms. The



final discrepancy indices were

$$R_1 = \sum ||F_o| - F_c| / F_o = 0.070$$

$$R_2 = (\sum w ||F_o| - F_c|^2 / \sum |F_o|^2)^{1/2} = 0.083$$

The estimated standard deviation of an observation of unit weight was 1.48.

A final difference Fourier map showed no peaks of chemical significance. The largest 7 peaks in the map were within ca. 1Å of the tungsten atoms and presumably reflect the inadequacies of the absorption correction.

A table of observed and calculated structure factors (11 pages) is available as supplementary material. See any current masthead page for ordering information.

#### RESULTS AND DISCUSSION

Reactivity. I is a highly reactive, air sensitive compound. It reacts in solution at room temperature with acetylene, dimethylacetylene, phenylacetylene, dimethylacetylenedicarboxylate, allene, ethylene and 1,3-butadiene. No reaction was observed with CO<sub>2</sub>. The above reactions were carried out in sealed tubes and monitored via <sup>1</sup>H NMR spectroscopy.

It is interesting to note that the corresponding Nb<sub>2</sub>(CSiMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> compound is comparatively inert, although it too is quite sensitive to moisture and oxygen.

Solid State Structure of W<sub>2</sub>(CSiMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>. The compound is composed of discrete molecules in the solid state. Each molecule possesses crystallographically imposed C<sub>1</sub> symmetry and the asymmetric unit consists of halves of two different molecules. The atomic positional and thermal parameters are given in Table I. The molecular structure of molecule I is shown in Figure 1 along with the atomic labelling scheme. A figure for molecule II is not given since the two molecules are essentially identical. The atoms of

molecule II are numbered using sets of numbers that follow those for molecule I. For example, the carbon atoms C(13), C(14),...C(24) correspond to C(1), C(2),...C(12) of molecule I. Bond distances and angles for both molecules are given in Tables II and III. A comparison of pertinent molecular dimensions for  $W_2(CH_2SiMe_3)_6$ , I, and  $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$  is given in Table IV.

The  $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$  molecule has a structure very similar to that of the niobium analog, although it may be noted that the two compounds are not isomorphous. Each metal atom is coordinated to two terminal alkyl groups and to two bridging alkylidyne groups. The C(1)-W(1)-C(1)' and C(5)-W(1)-C(9) planes are nearly perpendicular to each other and the three bonds to the bridging "carbyne" carbons are essentially coplanar. The only important differences between the  $Nb_2$  and  $W_2$  structures are due to the presence of the metal-metal bond in the tungsten compound.

The effects of the W-W bond on the molecular dimensions are very evident in three places. First, of course, there are the metal-metal distances themselves. The Nb-Nb distance, though it is as short, or shorter than, a number of Mo-Mo single bond distances,<sup>7</sup> which range from ca. 2.5 to ca. 3.3Å, is consistent with the absence of direct Nb-Nb bonding and is determined by the rather strong and short bonds to the bridging carbon atoms. The mean W-W distance, 2.535Å, is very much shorter and is consistent with the presence of a single bond between the tungsten atoms. W-W single bonds, like those between molybdenum atoms,<sup>7</sup> may vary enormously in length but the values observed here are near the short end of the range and leave no doubt that a W-W bond exists. Since  $W^{3+}$ -W bonds have lengths  $\leq 2.30$ Å and  $Re^{2+}$ -Re bonds (there are no well-defined  $W^{2+}$ -W bonds for comparison) are in the range 2.45-2.49Å, it is

not likely that there is significant multiple character to the W-W bond here.

The other two results of the M-M bond existing in I but not in its Nb analog are (a) a considerable contraction of the M-C-M angle in the W compound, and (b) an expansion of the ring angles at the W atoms. In the Nb compound the Nb-C-Nb angle is  $>90^\circ$  ( $94.4(4)^\circ$ ) while in the W compound the mean W-C-W angle is  $<90^\circ$  ( $84.5(10)^\circ$ ). Because the rings are planar the ring angles at the metal atoms are necessarily the complements of those at the bridging carbon atoms.

An interesting but somewhat puzzling feature of this structure is the apparent lack of symmetry in the bridges. This is suggested by the inequality of W-C bond lengths and also by the inequality in the W-C-Si angles. On the basis of the discrepancies in distances alone, one would not be justified in asserting that asymmetry exists, since the two independent discrepancies are only  $0.12\text{\AA}$  and  $0.08\text{\AA}$  while the esd in each individual bond length is ca.  $0.03\text{\AA}$ . However, the discrepancies in the angles are  $16^\circ$  in each case, while each individual angle has an esd of  $2^\circ$ , thus making it likely that there is some real asymmetry, although it may be a lot smaller than the discrepancies just mentioned would imply. Of course, very small discrepancies might result from intra- or intermolecular packing forces. This is an attractive idea, since there is no evident electronic reason to expect, or even rationalize, asymmetric bridging. In the case of the niobium compound there was similar, borderline evidence for asymmetry of the bridges.

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TABLE I. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS. <sup>a</sup>

ATOM	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
1	0.4686(1)	0.03122(6)	0.43717(7)	0.00737(9)	0.00237(3)	0.00312(4)	-0.0010(1)	0.0016(1)	0.00032(8)
2	0.0771(1)	0.01162(7)	-0.03707(8)	0.00915(11)	0.00424(5)	0.00330(5)	-0.0025(1)	0.0012(1)	0.00022(9)
3	0.5341(9)	0.1522(5)	0.5922(6)	0.0136(10)	0.0030(3)	0.0042(4)	-0.0006(9)	-0.001(1)	-0.0021(5)
4	0.1700(8)	0.0510(5)	0.4362(6)	0.0063(8)	0.0042(3)	0.0053(5)	0.0010(8)	0.000(1)	-0.0003(6)
5	0.6043(9)	0.1424(5)	0.3268(6)	0.0147(10)	0.0047(3)	0.0049(5)	-0.0050(10)	0.005(1)	0.0019(7)
6	0.0249(12)	0.1592(6)	0.0775(9)	0.0223(15)	0.0040(4)	0.0099(8)	-0.0021(12)	0.012(2)	-0.0015(9)
7	0.1170(11)	0.1131(6)	-0.1879(7)	0.0180(13)	0.0078(5)	0.0056(6)	-0.0004(13)	-0.002(1)	0.0059(8)
8	0.3275(11)	-0.0476(7)	0.0920(9)	0.0133(12)	0.0088(6)	0.0082(8)	0.0048(14)	-0.003(2)	-0.0007(12)
9	0.513(2)	0.068(1)	0.533(2)	5.2(7)					
10	0.470(3)	0.229(2)	0.533(2)	7.3(9)					
11	0.458(3)	0.144(2)	0.677(2)	7.1(9)					
12	0.693(3)	0.173(2)	0.625(2)	8.1(10)					
13	0.298(3)	0.062(2)	0.392(2)	6.4(8)					
14	0.147(3)	-0.043(2)	0.462(2)	9.3(11)					
15	0.047(4)	0.091(2)	0.366(3)	10.2(13)					
16	0.189(3)	0.105(2)	0.521(2)	8.3(10)					
17	0.500(3)	0.050(2)	0.366(2)	6.9(9)					
18	0.468(3)	0.192(2)	0.304(3)	9.0(11)					
19	0.710(3)	0.194(2)	0.394(2)	8.7(11)					
20	0.658(4)	0.132(3)	0.244(3)	13.5(16)					
21	0.014(3)	0.068(2)	0.025(2)	6.6(9)					
22	0.154(6)	0.169(3)	0.153(4)	19.2(25)					
23	0.007(6)	0.238(4)	0.020(4)	20.8(27)					
24	-0.097(6)	0.172(4)	0.126(5)	21.2(29)					
25	0.035(3)	0.044(2)	-0.150(2)	7.9(10)					
26	0.231(4)	0.159(2)	-0.118(3)	12.2(15)					
27	0.128(8)	0.118(5)	-0.284(6)	30.7(42)					
28	0.000(2)	0.189(4)	-0.200(6)	27.3(37)					

Table II. Bond Distances (Å)

Atoms	Distance	Atoms	Distance
W(1)-W(1)'	2.549(2)	Si(2)-C(8)	1.82(3)
-C(1)	1.85(3)	Si(3)-C(9)	1.93(3)
-C(1)'	1.97(2)	-C(10)	1.85(4)
-C(5)	2.13(3)	-C(11)	1.86(4)
-C(9)	2.05(3)	-C(12)	1.75(5)
W(2)-W(2)'	2.521(2)	S(4)-C(13)	1.97(3)
-C(13)	1.82(3)	-C(14)	1.87(7)
-C(13)'	1.90(3)	-C(15)	1.80(7)
-C(17)	2.11(4)	-C(16)	1.86(7)
-C(21)	2.13(3)	Si(5)-C(17)	1.84(3)
Si(1)-C(1)	1.91(3)	-C(18)	1.89(5)
-C(2)	1.88(3)	-C(19)	1.77(9)
-C(3)	1.93(3)	-C(20)	1.99(8)
-C(4)	1.92(3)	Si(6)-C(21)	1.83(4)
Si(2)-C(5)	1.87(3)	-C(22)	1.91(6)
-C(6)	1.88(3)	-C(23)	1.96(7)
-C(7)	1.90(4)	-C(24)	1.93(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.



Table III. Bond Angles (Degs).

Atoms		Angle		Atoms		Angle		Atoms		Angle	
W(1)	W(1)'	C(1)	50.2(8)	C(1)	S1(1)	C(4)	111(1)	C(13)	S1(4)	C(15)	117(3)
W(1)	W(1)'	C(1)	46.1(8)	C(2)	S1(1)	C(3)	108(1)	C(13)	S1(4)	C(16)	111(2)
W(1)	W(1)'	C(5)	124.4(8)	C(2)	S1(1)	C(4)	107(1)	C(14)	S1(4)	C(15)	109(3)
W(1)	W(1)'	C(9)	121.7(8)	C(3)	S1(1)	C(4)	111(2)	C(14)	S1(4)	C(16)	105(3)
C(1)	W(1)	C(1)'	96(1)	C(5)	S1(2)	C(6)	112(1)	C(15)	S1(4)	C(16)	98(3)
C(1)	W(1)	C(5)	110(1)	C(5)	S1(2)	C(7)	106(2)	C(17)	S1(5)	C(18)	117(2)
C(1)	W(1)	C(9)	114(1)	C(5)	S1(2)	C(8)	108(1)	C(17)	S1(5)	C(19)	123(3)
C(1)	W(1)	C(5)	114(1)	C(6)	S1(2)	C(7)	114(2)	C(17)	S1(5)	C(20)	98(3)
C(1)	W(1)	C(9)	107(1)	C(6)	S1(2)	C(8)	109(2)	C(18)	S1(5)	C(19)	117(3)
C(5)	W(1)	C(9)	114(1)	C(7)	S1(2)	C(8)	107(2)	C(18)	S1(5)	C(20)	98(3)
W(2)	W(2)'	C(13)	48.7(9)	C(9)	S1(3)	C(10)	110(1)	C(19)	S1(5)	C(20)	92(4)
W(2)	W(2)'	C(13)'	46.0(9)	C(9)	S1(3)	C(11)	112(2)	C(21)	S1(6)	C(22)	112(2)
W(2)	W(2)'	C(17)	120.4(9)	C(9)	S1(3)	C(12)	109(2)	C(21)	S1(6)	C(23)	108(3)
W(2)	W(2)'	C(21)	124.1(9)	C(10)	S1(3)	C(11)	110(2)	C(21)	S1(6)	C(24)	113(2)
C(13)	W(2)	C(13)'	95(1)	C(10)	S1(3)	C(12)	109(2)	C(22)	S1(6)	C(23)	121(3)
C(13)	W(2)	C(17)	112(1)	C(11)	S1(3)	C(12)	108(2)	C(22)	S1(6)	C(24)	100(2)
C(13)	W(2)	C(21)	113(1)	W(1)'	C(1)	W(1)	84(1)	C(23)	S1(6)	C(24)	103(3)
C(13)	W(2)	C(17)	108(1)	W(1)	C(1)	S1(1)	146(2)	W(2)'	C(13)	W(2)	85(1)

Table III. Bond Angles (Degs).

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(13) W(2) C(21)	111(1)	W(1)' C(1) S1(1)	130(2)	W(2) C(13) S1(14)	145(2)
C(17) W(2) C(21)	115(1)	W(1) C(5) S1(2)	128(2)	W(2)' C(13) S1(4)	129(2)
C(1) S1(1) C(2)	109(1)	W(1) C(9) S1(3)	124(1)	W(2) C(17) S1(5)	121(2)
C(1) S1(1) C(3)	110(1)	C(13) S1(4) C(14)	115(2)	W(2) C(21) S1(6)	131(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Average Bond Lengths (Å) in  $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$ ,  $W_2(CH_2SiMe_3)_6$ ,<sup>a</sup> and  $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$ .<sup>b</sup>

Compound	Bonds	Average	Range
$W_2R_2'R_4$	W-W	2.535	2.521(2)-2.549(2)
	W-C <sub>t</sub>	2.11(4)	2.05(3)-2.13(3)
	W-C <sub>b</sub>	1.89(7)	1.82(3)-1.97(2)
	Si-C	1.88(6)	1.75(5)-1.99(8)
$W_2R_6$	W-W	2.255(2)	2.254(2)-2.255(2)
	W-C <sub>t</sub>	2.14(6)	2.03(4)-2.23(3)
	Si-C	1.89(6)	1.80(5)-2.04(4)
$Nb_2R_2'R_4$	Nb-Nb	2.897(2)	—
	Nb-C <sub>t</sub>	2.160(9)	—
	Nb-C <sub>b</sub>	1.975	1.954(9)-1.995(9)
	Si-C	1.86(1)	—

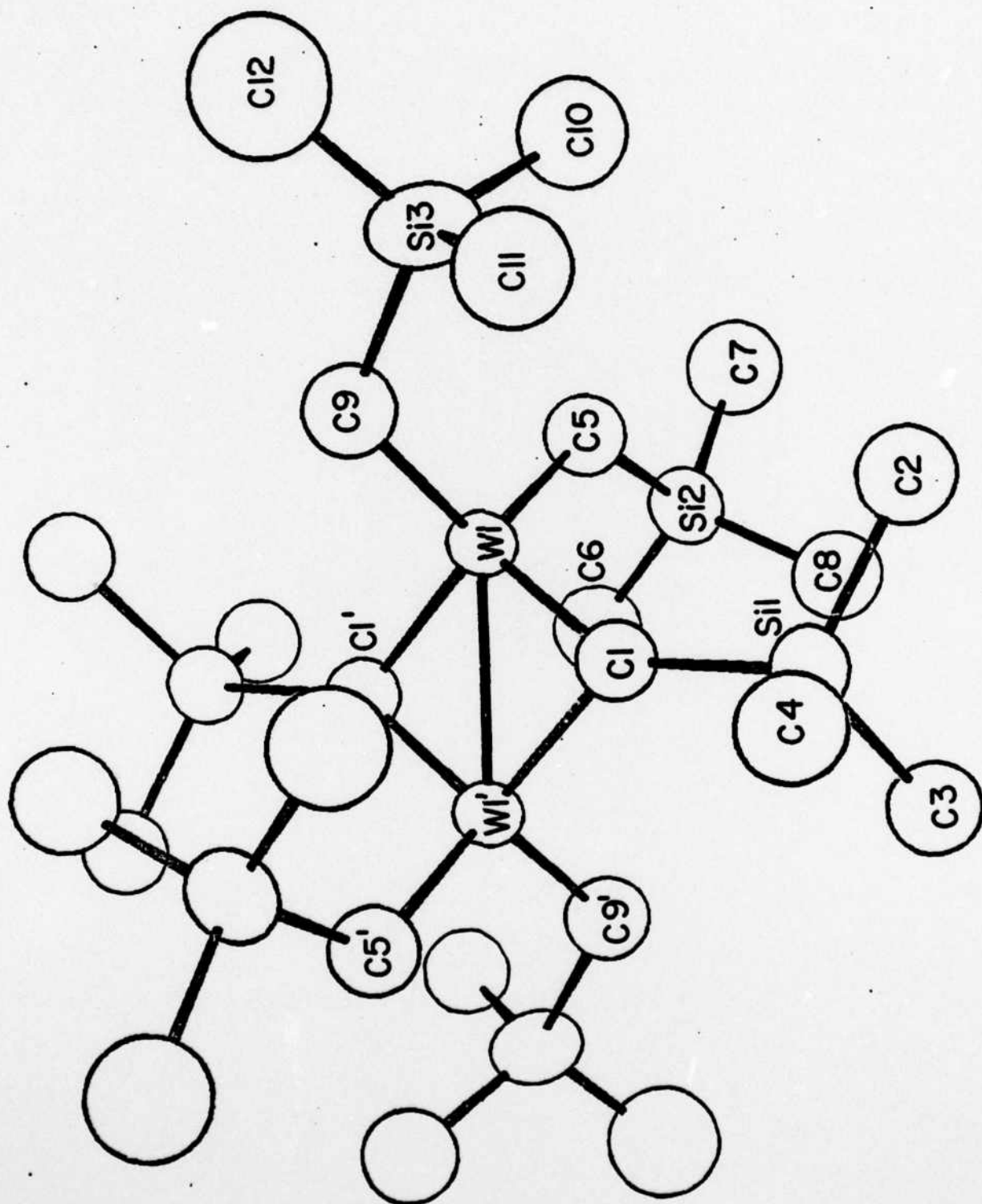
<sup>a</sup>Cf. Ref. 2

<sup>b</sup>Cf. Ref. 4.

<sup>c</sup>R' = CSiMe<sub>3</sub>, R = CH<sub>2</sub>SiMe<sub>3</sub>, C<sub>t</sub> = terminal carbon, C<sub>b</sub> = bridging carbon.

Numbers in parentheses are either the standard deviation from the mean bond lengths or the estimated standard deviations of the individual bond lengths.

Figure 1. A view of Molecule I using 40% probability ellipsoids and showing the atom labelling scheme. Molecule II is essentially identical.



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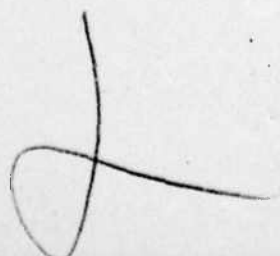
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